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SYNTHESIS AND EMERGING IDEAS

# Hydrogen peroxide production driven by UV-B in planktonic microorganisms: a photocatalytic factor in sea warming and ice melting in regions with ozone depletion?

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**Abstract** UV-B radiation activates the synthesis of hydrogen peroxide from water and oxygen in many protein kinds, which having been discovered initially in antibodies, has been so far applied to explore new mechanisms in relation to immune defence. As shown here, the natural association of this common photocatalysis and catalase transforms UV-B photons into heat in a cyclic reaction that represents in biology a basic defence mechanism against UV-B radiation and cold, the activity of which drives the buoyancy and production of planktonic microorganisms in cold oceans. Moreover, given that UV-B radiation reaching the Earth's surface depends mainly on changes in the ozone layer, that defence mechanism over-activated by ozone depletion in microorganisms gathered at the top layer of the water column during seasonal production could result in accelerated sea ice melting, surface warming and ecosystem changes, such as is happening at high latitudes. Thus, one concludes that UV-B-driven photoproduction and decomposition of hydrogen peroxide in plankton can be a new, hidden biogeochemical process under control of the ozone layer with important effects on the ecosystem and climate.

**Keywords** Artic ice melting · Climate change · Hydrogen peroxide · Ozone depletion · Sea warming · UV-B radiation

## Introduction

The oxidation of water ( $\text{H}_2\text{O}$ ) by dioxygen ( $\text{O}_2$ ) yielding hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in antibodies exposed to ultraviolet-B radiation (UV-B) (280–320 nm) is an amazing photocatalysis discovered a decade ago (Wentworth et al. 2000, 2001). Of note, such a UV-B-driven process, hereafter referred to as water photo-oxidation (WPO), cannot take place in antibodies under natural conditions. However, preliminary studies showed that in the absence of UV-B,  $\text{H}_2\text{O}_2$  is also produced from  $\text{H}_2\text{O}$  and singlet  $\text{O}_2$  ( $^1\text{O}_2^*$ ) (Wentworth et al. 2000, 2001), which is an activated species produced in inflammatory processes. Due to the fact that  $\text{H}_2\text{O}_2$  is a potent microbicide, the latter  $\text{H}_2\text{O}_2$  production by  $^1\text{O}_2^*$  in the absence of UV-B—the so-called antibody-catalyzed water oxidation pathway—was subsequently featured as a new chemical arm to immune defence (Nieva and Wentworth 2004), which, however, has been questioned by others (Parren et al. 2003).

While the initial interest in the antibody-catalyzed water oxidation pathway (that is, water oxidation by  $^1\text{O}_2^*$ ), has progressively declined, the role of the initially discovered WPO still remains unsolved.

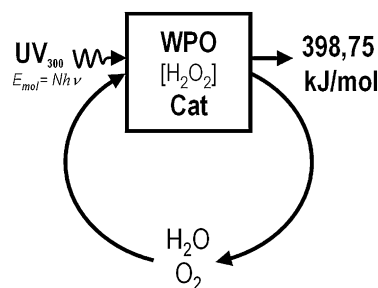
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Interestingly, WPO is not unique for antibodies, but rather a common activity being catalyzed with variable efficiency in most proteins usually found in the laboratory, such as  $\beta$ -lactoglobulin,  $\beta$ -galactosidase, ovalbumin, trypsinogen, lectins, bovine serum albumin, and  $\alpha$ -lactalbumin (Wentworth et al. 2000). Extrapolating these data, no doubt there will be countless proteins actually photoproducing  $\text{H}_2\text{O}_2$  in microorganisms subjected to UV-B in natural conditions. Moreover, given that microorganisms living under solar UV-B constitute a large part of the Earth's biomass, that common WPO could be a global bioactivity which plays a role in nature.

### In search of a role for WPO

WPO is a reaction of catalytic nature, whose initial rates decline due to reversible inhibition by its  $\text{H}_2\text{O}_2$  product (Wentworth et al. 2001). Thus, in the presence of enough catalase activity, WPO proceeds at the maximal, initial rate. Studying the effect of catalase on WPO has not been arbitrary: catalase being the fastest and most ubiquitous activity in biology (Loew 1900; Aebi 1985) evolved to remove  $\text{H}_2\text{O}_2$ , a well-known toxic compound for all microorganisms, which is produced in many metabolic processes. Thus, wherever WPO occurred and whatever its role was, catalase must always be present; otherwise, WPO would eventually kill living cells.

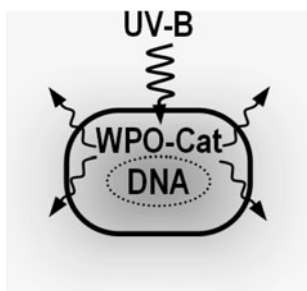
As a result of the virtual association of WPO and catalase in living cells (hereafter referred to as WPO-Cat), WPO product ( $\text{H}_2\text{O}_2$ ) is transformed into WPO substrates ( $\text{O}_2$  and  $\text{H}_2\text{O}$ ), so all UV-B energy fuelling WPO at maximal rate is instantly transformed into heat (Fig. 1). The action spectrum of WPO extends from 270 to 320 nm (Wentworth et al. 2001), a range including the spectrum of the biologically active UV-B (BA-UV-B) reaching the Earth's surface (Madronich and Flocke 1997). According to the photoequivalence law, one einstein of 300 nm—the typical wavelength of the BA-UV-B—yields 398.75 kJ per mol of  $\text{H}_2\text{O}_2$  produced and decomposed (Fig. 1), which is 13 times more than the 30.5 kJ/mol produced in ATP hydrolysis, one of the most exothermic reactions in cells. Indeed, WPO-Cat activated by BA-UV-B plays a cyclic reaction that is by far the most exothermic in biology. Moreover, WPO-Cat using and producing  $\text{H}_2\text{O}$  and  $\text{O}_2$  at



**Fig. 1** Water photooxidation-catalase (WPO-Cat) at molecular level. WPO product ( $\text{H}_2\text{O}_2$ ) is decomposed by catalase (Cat) into WPO substrates ( $\text{O}_2$  and  $\text{H}_2\text{O}$ ) at maximal rate in a cyclic reaction. No chemical compound is produced at the virtual WPO-Cat complex (represented into a box), so all the energy of one einstein of 300 nm (twisted arrow) is transformed into heat (398.75 kJ/mol) ( $\Delta E_{\text{mol}} = Nh\nu$ , where  $N$  is Avogadro number,  $h$ : Planck constant,  $\nu$ : frequency)

maximal rate, is a cheap, clean and efficient process of delivering heat (i.e.  $\text{H}_2\text{O} + \text{O}_2 + h\nu \rightarrow \text{H}_2\text{O} + \text{O}_2 + \Delta Q$ ) to living cells.

WPO in the test tube is activated by UV-B irradiation of  $8 \text{ W/m}^2$  (Wentworth et al. 2001), which is in the order of magnitude of that of solar origin that reaches the Earth's surface throughout the evolution. Even so, WPO has been thus far considered as a reaction with no apparent biological role, possibly because of its discovery in proteins that cannot be physiologically activated by solar UV-B. However, given that all current life forms come from a common ancestor (Theobald 2010), one can formally postulate that such WPO originates in ancient aquatic microorganisms which, living subjected to solar UV-B, generated all current forms of life, where WPO still persists in many of them as an old legacy. If that is true, WPO surely preceded and contributed to the evolution of catalase, which occurred in primitive microorganisms under  $\text{H}_2\text{O}_2$  pressure about 2.5–3 Gyrs ago (McKay and Hartman 1991), thus leading to the WPO-Cat beginning just when the Earth was a gelid planet subjected to high levels of solar UV-B (Kasting and Siefert 2002; Lenton et al. 2004). Certainly, the climate system is powered by the incoming solar energy, which ultimately becomes heat at the Earth's surface (Kiehl and Trenberth 1997). In turn, the climate system is essential to sustain the life. However, by means of WPO-Cat, planktonic microorganisms obtain an individual heat source, which being independent of the climate system, would be able to maintain metabolic



**Fig. 2** WPO-Cat at cellular level. Heat production (*shadow and small twisted arrows* representing longwave radiation) from UV-B photons (*big twisted arrow*) by WPO-Cat in a microorganism (*oval*) protects its DNA from harmful effects of UV-B while increasing its metabolic rate

processes in extremely cold conditions (Fig. 2), such as those existing 2.5–3 Gyrs ago, that is, before or at the beginning of the climate system, during glaciations and currently at high latitudes. On the other hand, UV-B has well known harmful effects on microorganisms (Häder 2000; Sinha and Häder 2002), so natural UV-B absorbers at the sea surface, such as dissolved organic carbon (DOC), are believed to protect planktonic microorganisms. Besides DOC, plankton is also an important UV-B absorber at the sea surface (Häder 1997). Therefore, in addition of producing heat for metabolic processes, WPO-Cat in cell membranes, cytoplasm and nucleus (i.e. nucleoproteins) (Fig. 2) would represent an efficient shield in microorganisms to protect their nucleic acids from harmful effects of UV-B.

### WPO-Cat: actually an adaptive mechanism against UV-B?

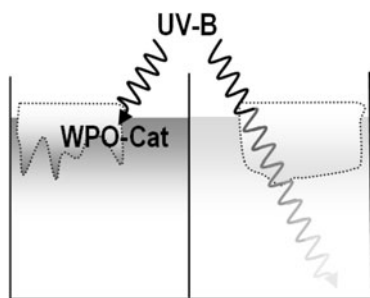
The emerging idea of WPO-Cat as a universal defence mechanism in microorganisms against UV-B and cold is logical. However, its existence is not supported at first glance by data showing the adverse effects of short-term exposure to UV-B—which is the one predominating in a mixed water column—on planktonic microorganisms (Herndl et al. 1993). In defence of WPO-Cat, it is well-known that planktonic microorganisms, like many others, express catalase activity in response to  $H_2O_2$  exposure (Morgan et al. 1986; Angel et al. 1999). Thus, if  $H_2O_2$  was actually photoproducted in plankton, catalase activity will be induced by UV-B (i.e. daylight) and suppressed in the

darkness. In fact, the expression of catalase activity in microorganisms has been shown to follow natural daylight fluctuations, becoming maximal at noon and minimal at dawn and sunset (Angel et al. 1999). However, to study the effects of short-term exposure to UV-B on plankton, samples must be placed in the darkness for a while in order to compare the activity in samples exposed again to UV-B with that in samples that continue in the darkness. As catalase is suppressed in the darkness (Angel et al. 1999), the detrimental effects observed in microorganisms suddenly brought from darkness to normal-higher levels of UV-B ( $1\text{--}3\text{ W/m}^2$ ) (Herndl et al. 1993) could be due to the well-known toxic effects of  $H_2O_2$  (Abele-Oeschger et al. 1997; Angel et al. 1999). From this perspective, the existence of WPO-Cat in microorganisms is consistent with the results of Herndl et al. (1993). Furthermore, their data showing that the activity in samples exposed to low levels of UV-B ( $>0.2\text{ W/m}^2$ ) was higher than in control samples (Herndl et al. 1993) support strongly that the deleterious effects of acute UV-B exposure on planktonic microorganisms were due to  $H_2O_2$  photoproduction rather than to DNA damage. That is, when exposed to a low-level of UV-B or following natural daylight fluctuations, a parallel expression of catalase activity in microorganisms (Angel et al. 1999) avoids  $H_2O_2$  toxicity while producing beneficial heat from UV-B.

### The impact of WPO-Cat on sea ice

In high latitude regions, it is well-known that aquatic microorganisms enclosed by floating ice during winter are released in spring to the water–ice interface, where they initiate their seasonal proliferation. Given its high-power of penetration, UV-B is actually capable of reaching microorganisms living below ice up to 3–4 m thick (Vincent et al. 1998; Lesser et al. 2004). The albedo of snow and ice is high, but reaches its lowest levels during spring and summer (i.e. during seasonal proliferation). On the other hand, below an ice layer, the water column is very stable, so the heat produced just at the water–ice interface is very steady and efficient. Certainly, floating ice populated by microorganisms at its water–ice interface will melt faster under identical climate and solar irradiation conditions than floating

ice lacking microorganisms (Fig. 3). Therefore, while shielding microorganisms against UV-B and cold, WPO-Cat is an ice melting accelerant, so playing a primary role in seasonal production at high latitudes. Note that floating ice will lose thickness as heat produced by WPO-Cat is released at ice–water interface (Fig. 3), so the thinner the floating ice layer becomes, the more the UV-B reaches the ice–water interface, and so on. Since UV-B reaching the ice–water interface depends mainly on changes in the ozone layer, the rates of ice thickness loss due to WPO-Cat could be exponential if plankton proliferation occurs in conditions of ozone depletion. As a matter of fact, Arctic sea ice thickness has been recently shown to be severely affected during the last three decades (Kwok et al. 2009), so overall mean winter thickness of 3.64 m in 1980 can be compared to a recent 1.89 m, an astonishing decrease of 1.75 m (Kwok and Rothrock 2009), just when severe ozone depletion of anthropogenic origin has led to a dramatic increase in UV-B in this region (Madronich et al. 1998; McKenzie et al. 2007). Certainly, Arctic sea ice extension loss could be accounted for by sea warming at the ice borders. However, Arctic sea ice thickness loss in colder areas far from ice borders must involve some factor acting in the ice–water interface, such as WPO-Cat over-activated by severe ozone depletion during the huge seasonal proliferation that takes place below Arctic sea ice (Fig. 3).



**Fig. 3** WPO-Cat at macroscopic level: effects on ice melting and sea surface temperature. (*Shadow intensity* indicates higher plankton concentration and temperature and *dotted block* represent floating ice). *Left*: WPO-Cat in microorganisms gathered at the top layer of the water column concentrates heat from UV-B at water–ice and water–air interfaces, so leading to floating ice thickness loss and sea warming. *Right*: In the lack of plankton playing WPO-Cat, the gradual attenuation of UV-B results in slower ice melting and colder surface under the same solar irradiance and climate conditions

### The impact of WPO-Cat on sea surface temperature and plankton production

The absorption of UV-B underwater is well-known to depend strongly on the concentration of planktonic microorganisms, which, in natural conditions, concentrate at the top layer of the water column. Hence, UV-B is either quickly absorbed in productive coastal waters or penetrates much deeper in oligotrophic open oceans (Häder 1997). As shown in Fig. 3, WPO-Cat in plankton proliferating at sea surface would perform as a filter for UV-B, thus concentrating its energy at the top layer of the water column. Certainly, there are UV-B absorbers at the sea surface other than WPO, such as DOC, which compete with plankton to absorb similar UV-B wavelengths. However, UV-B absorption by WPO-Cat could predominate if planktonic microorganisms concentrate heavily at the very sea surface, such as commonly occurs during seasonal plankton production (i.e. plankton blooms). Plankton's dry weight is mostly protein, which is one of the most active UV-B chromophores in nature (Brown 1980). Indeed, such a thick protein film at the sea top will absorb almost all UV-B reaching the surface of eutrophic waters, a large part of which becomes heat due to WPO-Cat as well as molecular relaxation processes in proteins (Brown 1980). On the other hand, DOC and other UV-B absorbers at the extracellular space come mainly from plankton and follow a similar distribution, so the remaining UV-B not absorbed by planktonic proteins will also contribute to heat production at sea surface. In fact, the same UV-B wavelengths that activate WPO-Cat in microorganisms also activate the  $H_2O_2$  photoproduction by DOC at the extracellular space (Abele-Oeschger et al. 1997; Yocis et al. 2000), which could represent a soluble form of WPO-Cat. To sum up, UV-B disappearing suddenly in eutrophic waters would mostly become heat. Besides light and nutrients, temperature is an essential factor in the 'integrated growth environment' (IGE) that sustains plankton production (Behrenfeld et al. 2008). For instance, the transformation of a UV-B irradiance of  $1 \text{ W/m}^2$  into heat at the very sea surface could theoretically increase by one degree the temperature of the first millimetre of a cold water column in 1 h. So, WPO-Cat could be essential to achieve the IGE for plankton production at sea surface or below ice in cold oceans.

On the other hand, it is very important to note that microorganisms playing WPO-Cat will lose density due to the fact that the heat from UV-B is delivered inside them (Fig. 2). Water density increases at lower temperatures, reaching a maximum at 4° C. Thus, in a cold, non-stratified water column, such as in high latitudes, the more the microorganisms play WPO-Cat, the higher they will rise, which thus accumulate at the water–air or the water–ice interfaces. The higher the plankton concentration is here, the bigger the UV-B absorption (Häder 1997) and heat production become, which in turn results in further plankton production, and so on. WPO-Cat would thus drive the buoyancy of microorganisms, so contributing further to a suitable IGE for plankton production in cold oceans. Those plankton species being more ready to play WPO-Cat would thus be more thermophilic and ‘UV-B-philic’ than those ones less ready to play WPO-Cat, which would be rather cryophilic and ‘UV-B-phobic’. So, WPO-Cat over-activated by higher UV-B levels would promote the expansion of the thermophilic plankton species at the expense of cryophilic ones in cold oceans, which in fact has been the main ecosystem change observed in high latitudes undergoing severe ozone depletion during recent decades (Hays et al. 2005). To sum up, while avoiding harmful UV-B, WPO-Cat driving microorganisms’ buoyancy is also essential to achieve a suitable IGE for plankton production in cold oceans, so playing a key role in the evolution of marine ecosystem in cold climate conditions.

### WPO-Cat and the climate system

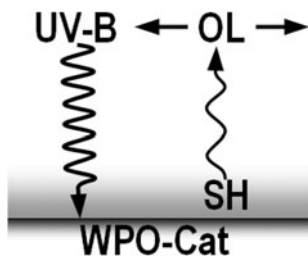
Heat produced by WPO-Cat from UV-B at the water–air interface is mostly transferred to the air, which would surely have an effect on the mixed layer temperature. WPO-Cat’s natural scenarios are cooler, seasonal oceans in high latitudes. In evaluating here the climatic impact of WPO-Cat, it is important to note first that WPO is a heat source at the very sea surface, thus contributing to the sensible heat flux (SH) of the climate system (Kiehl and Trenberth 1997). Otherwise, the UV-B not absorbed by WPO-Cat at the water–air interface (Fig. 3, left) will result in latent heat flux (LH), as well as in the longwave flux (LW) (i.e. surface heat flux). The shortwave surface flux (SW) generates the three SH, LH and

LW, in such way that in any latitude  $SW = SH + LH + LW$  (Kiehl and Trenberth 1997), and in case of UV-B,  $SW_{UV-B} = SH_{UV-B} + LH_{UV-B} + LW_{UV-B}$ . SH represents only 14% of SW (Kiehl and Trenberth 1997), but plays an important role in atmospheric circulation and short-term regional climate (i.e. weather). Climate system’s energy budget from Kiehl and Trenberth (1997) applies to 0° latitude (i.e. tropics) (<http://www.physicalgeography.net/fundamentals/7j.html>). Values at 70° latitude (i.e. both Poles) come from multiplying values at 0° latitude per  $\cos 70^\circ$ . Thus, SW is approximately 50 W/m<sup>2</sup> at 70° latitude, 14% of which (i.e. 7 W/m<sup>2</sup>) is SH. According to Madronich et al. (1995), 1% decrease in the total ozone column near 300 DU at a zenithal solar angle of 70° leads to an increase in UV-B of 8 mW/m<sup>2</sup>. However, UV-B levels grow exponentially at ozone losses bigger than 30%, (Madronich et al. 1998), so current ozone depletion frequently achieving 30% at the North and 60% at the South during recent decades have resulted in UV-B increases of 50 and 150%, that is, 0.24 and 0.72 W/m<sup>2</sup>, respectively. Plankton production at a determinate place is deemed as unpredictable. However, given that WPO-Cat pushes upwards the planktonic microorganisms while providing heat for achieving a suitable IGE in cold oceans, UV-B will increase the probability of plankton production, especially in those zones exposed to higher levels. In turn, initial plankton production driven by UV-B would absorb more UV-B, so increasing further plankton production, and so on. What is more, the higher the UV-B levels, the more the UV-B-phobic (i.e. cryophilic) plankton species have been replaced by UV-B-philic ones (see above). So, in current ozone depletion conditions, a large part of  $SW_{UV-B}$  would become  $SH_{UV-B}$  by WPO-Cat during seasonal production at high latitudes in detriment of  $LH_{UV-B}$  and  $LW_{UV-B}$ . If, for instance, 80% of the  $\Delta SW_{UV-B}$  (i.e. 0.24 and 0.72 W/m<sup>2</sup>) became  $SH_{UV-B}$ , over-activated WPO-Cat will increase the SH at 70° latitude (i.e. 7 W/m<sup>2</sup>) by 3 and 8%, respectively, which could actually result in significant changes in atmospheric circulation and surface warming at decadal scale. Indeed, photochemical ozone losses leading to changes in tropospheric circulation have been considered as the main cause of near-surface warming at high latitudes (Hartmann et al. 2000; Thompson and Solomon 2002; Gillett and Thompson 2003). As it is



clear that changes in ozone layer have a primary impact on the  $SW_{UV-B}$  (Madronich and Flocke 1997; McKenzie et al. 2007), recent changes in tropospheric circulation and near-surface warming could be due to the increases in  $SH_{UV-B}$  caused by WPO-Cat over-activation (Fig. 4), which would be thus the culprit for the sharp seasonal episodes of sea surface warming leading to the collapse of ice shelves at the South and ice melting at the water–ice interface leading to severe thickness loss undergone by the Arctic sea ice during recent decades. For instance,  $0.07 \text{ W/m}^2$  (which is the 30% of the UV-B increase at the Arctic) becoming heat at water–ice interface in one area of  $10^5 \text{ km}^2$  (i.e. an spherical ring 8 km wide at  $70^\circ$  latitude) during 1 week would produce at the water–ice interface 4.24 PJ, a little more than 1 megaton, which is about 80 times the 13 kilotons of an atomic bomb in the Second World War. Indeed, the power of the tiny should not be underestimated.

UV-B irradiation increases at lower latitudes, so WPO-Cat will protect plankton against it. However, in less dense warmer waters, WPO-Cat would neither drive the microorganisms' buoyancy nor be essential to achieve a suitable IGE. That is, microorganisms do not behave as UV-B-philic in permanently stratified oceans regions at middle-low latitude. Here, microorganisms do not gather at the surface to proliferate by the UV-B call as in high latitudes, so that much less UV-B is absorbed by WPO-Cat, whose weak heat output would not be concentrated at the top layer of the water column (Fig. 3). As a result,  $SH_{UV-B}$  due to WPO-Cat would decrease at the expense of



**Fig. 4** WPO-Cat at global level acting as a link between the ozone layer circulation and surface climate. UV-B driven by the ozone layer (OL) activates WPO-Cat at sea surface, whose sensible heat flux (SH) results in surface warming, changes in tropospheric circulation and energy waves that in turn drive the OL circulation

increases in  $LH_{UV-B}$  and  $LW_{UV-B}$  in middle-low latitudes. Moreover, given that ozone depletion is only 3% in middle latitudes and virtually none at the tropics, increases in  $SW_{UV-B}$  are here negligible. At first glance, WPO-Cat would play only a marginal role in this climate scenario. However, whenever sea surface becomes cooler, which happens frequently during seasonal production at middle and low latitudes, microorganisms will behave again as UV-B-philic. In the presence of appropriate light and nutrients, plankton production could be considerably activated by WPO-Cat, which absorbing a large part of 'normal' UV-B (i.e.  $1\text{--}2 \text{ W/m}^2$ ) will increase  $SH_{UV-B}$  and affect the regional weather (Fig. 4). In fact, changes in near-surface climate and weather have been shown to be tightly-linked to the ozone layer circulation by means of energy waves which transfer heat from sea surface to the stratosphere (Baldwin et al. 2003; Reichler et al. 2005; Shaw and Shepherd 2008) (Please, compare the Fig. 1 from Shaw and Shepherd 2008, [http://www.nature.com/ngeo/journal/v1/n1/fig\\_tab/ngeo.2007.53\\_F1.html](http://www.nature.com/ngeo/journal/v1/n1/fig_tab/ngeo.2007.53_F1.html) to Fig. 4). Furthermore, in tropical waters undergoing natural oscillations in temperature and being naturally exposed to the highest levels of UV-B, seasonal blooms driven by WPO-Cat could suddenly produce huge increases in  $SH_{UV-B}$ . Now, 1 megaton would be released to the troposphere in only 12 h if  $1 \text{ W/m}^2$  is transformed into heat by WPO-Cat in one area of  $10^5 \text{ km}^2$  (i.e.  $1000 \times 100 \text{ km}$ ). Indeed, such episodic WPO-Cat could play a key role in the origin of well-known destructive meteorological phenomena that occur during seasonal production in tropical waters.

From a different perspective, increases in UV-B due to a mean ozone depletion of 5% would represent at global level a radiative forcing of only  $0.08 \text{ W/m}^2$ , which compared to the radiative forcing of  $1.5 \text{ W/m}^2$  due to  $\text{CO}_2$  is almost negligible. Thus, radiative forcing due to increased UV-B levels by ozone depletion plays a very small role in global warming, while increases in SH due to WPO-Cat over-activation by ozone depletion would indeed play a major role in regional warming. Still, data from Hartmann et al. (2000) support that surface warming related to zone depletion at high latitudes (i.e. increases in  $SH_{UV-B}$  due to over-activated WPO-Cat) and greenhouse effect could interact to produce rapid climate change.

## WPO-Cat: why unknown thus far?

Whereas modest heat fluxes coming from the degradation of chemical energy originally fixed by photosynthesis have been detected in aquatic ecosystems (Pamatmat 2003), it is paradoxical that such a powerful WPO-Cat remained thus far unknown. Certainly,  $\text{H}_2\text{O}_2$  detection has made WPO discovery possible in isolated proteins (Wentworth et al. 2000, 2001). But in microorganisms,  $\text{H}_2\text{O}_2$  is a potent microbicide being instantly transformed into water and oxygen by catalase activity (Fig. 1). In other words,  $\text{H}_2\text{O}_2$  behaves as a short-lived intermediate in living cells, which is undetectable by current methods, unless catalase activity is removed. In fact, when studying the effect of catalase on WPO in antibodies, Wentworth et al. (2001) had to develop a procedure to remove the added catalase in order to measure the  $\text{H}_2\text{O}_2$  output. Accordingly, to establish whether  $\text{H}_2\text{O}_2$  is photoproduced in microorganisms, plankton samples should be placed in the darkness enough time to suppress catalase activity (Angel et al. 1999), and then measuring  $\text{H}_2\text{O}_2$  after a short exposure to UV-B (see above). However, due to the fact that  $\text{H}_2\text{O}_2$  produced in aquatic environments is highly unstable,  $\text{H}_2\text{O}_2$  measurements are always performed immediately (Abele-Oeschger et al. 1997; Yocis et al. 2000). By doing so, only traces of  $\text{H}_2\text{O}_2$  produced at the extracellular space by UV-B photoactivation of DOC have been thus far detected (Abele-Oeschger et al. 1997; Yocis et al. 2000), whilst massive  $\text{H}_2\text{O}_2$  generation by WPO in microorganisms would have systematically escaped experimental detection. On the other hand, SH is one of the most variable factors in the climate system showing deviations of  $\pm 25\%$  (Kiehl and Trenberth 1997), so changes in  $\text{SH}_{\text{UV-B}}$  due to WPO-Cat would be hidden by that natural variability. To sum up, WPO-Cat lacking a measurable chemical product in microorganisms would be an extremely elusive activity, whose climate impact would have been either overlooked or attributed to other causes.

## Conclusion

Considering that UV-B and cold are universal conditions in the origin and evolution of the life on Earth, much more could be said about the WPO-Cat's role in the biosphere and climate not only at present

but also in the past. For now, on the basis of all the above, here one finally concludes that the recently discovered WPO powered by UV-B, as catalyzed in planktonic microorganisms, could be a hidden biogeochemical process under control of the ozone layer with important effects on marine ecosystems and climate which, given the current global crisis, should be brought to light without delay.

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